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THE POLING TIME DEPENDENCE OF THE FIELD INDUCED PHASE TRANSITION--ETC(U)  
MAR 80 J I SCHEINBEIM, C H YOON, K D PAE N00014-75-C-0540  
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*d<sub>31</sub> 31*

*e<sub>31</sub> 31*

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Synopsis

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Abstract

We have examined the poling time dependence of the field induced phase transition (from phase II to polar phase II) of biaxially oriented poly(vinylidene fluoride) films by x-ray methods. These results were compared with the poling time dependence of the piezoelectric response ( $d_{31}$  and  $e_{31}$ ) determined using a Piezotron Model U (Toyo Seiki, Tokyo). The piezoelectric response shows an initial rapid increase with poling time followed by a slow increase as the poling time increases. The x-ray results show that the field induced phase transition is time dependent, and occurs first for those crystallites with their a axes perpendicular to the film surface. Crystallites with a in the plane of the film transform at a much slower rate. The data indicate that the poling time dependence of  $d_{31}$  and  $e_{31}$  (and, presumably, film polarization) are dependent on the transition rates.

Introduction

Previous investigations of the dependence of the polarization of poled poly(vinylidene fluoride) (PVF<sub>2</sub>) films on poling time<sup>1-7</sup> indicate that the polarization occurs in two stages. First, a rapid increase in polarization occurs, followed by a slowly increasing polarization. Some investigators reported that the fast increase occurred within

seconds, while others reported that it occurred within minutes of the application of the poling field. Most agreed that the slow increase occurred over a time period of hours. Other data implied that the rate of increase in polarization depended on poling temperature, with the maximum possible film polarization dependent only on poling field.

Although the poling time dependence of the film polarization has been well established, the mechanisms responsible for the initial rapid increase or the following slow increase have not been determined. However, it has been suggested that the polarization is nonuniform and an increase in the uniformity of polarization may be responsible for the slow increase.<sup>3,8</sup>

In this laboratory, we have been investigating the mechanisms responsible for the observed polarization of  $\text{PVF}_2$  films, using piezoelectric activity as a measure of film polarization. This was done by examining the changes occurring in the crystalline regions of the poled films using x-ray diffraction methods and by attempting to correlate the crystallographic changes with changes in piezoelectric response. Previous work<sup>9-11</sup> has shown that the poling of biaxially oriented  $\text{PVF}_2$  films containing primarily the nonpolar phase II polymorphic crystal form produces a phase transition from phase II to a polar crystal form called polar phase II (or II\*). It has been suggested that this oriented polar phase II crystalline material is responsible for the film polarization. Using  $d_{31}$  and  $e_{31}$ , the piezoelectric strain and stress constants respectively, as measures

of film polarization, we found a strong correlation between the amount of material converted from phase II to polar phase II and film polarization for films poled for several hours.<sup>11</sup> We, therefore, decided to investigate the possibility of a poling time dependence for the previously observed phase transition and, if such a time dependence existed, attempt to correlate it with the time dependent changes in film polarization.

### Experimental

Biaxially oriented, 25 micron thick samples of capacitor grade Kureha PVF<sub>2</sub> film were electroded with silver paste. The samples were then poled at various poling times (6 sec, 30 sec, 1 min, 3 min, 10 min, 30 min, 1 hr and 2 hrs). The poling field used was  $2 \times 10^6$  V/cm and the poling temperature was 23°C. In this study, a conventional, two-terminal, poling technique was used. The output of a high voltage D.C. supply (5 KV) was connected through a switch across the sample. Poling was done under vacuum, with a pressure  $\sim 10^{-5}$  torr. Piezoelectric measurements were performed using a Toyo Seiki Piezotron.

After the electrical measurements were completed, the electrode material was removed and wide angle x-ray diffraction scans (using CuK<sub>α</sub> radiation) were taken in reflection and transmission mode.

### Results and Discussion

#### (a) Electrical Measurements

A plot of the complex piezoelectric stress constant,  $e_{31}^*$  versus poling time is shown in Fig. 1.  $e_{31}^*$  exhibits the expected poling time dependence: a fast increase occurring during the first several seconds

followed by a much slower increase as the poling time increases to two hours. In Fig. 2, the complex piezoelectric stress constants,  $d_{31}^*$ , obtained using different poling times are plotted. A similar time dependence can be observed. The data indicate that both  $e_{31}^*$  and  $d_{31}^*$  reach ~80% of their final (2 hour) value in less than 10 seconds.

(b) X-Ray Measurements

The wide angle x-ray diffraction scans (reflection and transmission) of PVF<sub>2</sub> films poled for different times are shown over a limited range of Bragg angle (16°-24°) in Figs. 3 and 4. The diffraction scans show the variation in diffracted intensity with poling time for the most important reflections (100), (020) and (110) from phase II and the (110), (200) reflection from phase I. It is important to realize that a comparison of reflection and transmission scans permit a comparison of the response of different crystallites (with different orientations to the film surface) to poling. The reflection scans show the previously reported changes in x-ray reflections consistent with the phase transition from phase II to polar phase II<sup>(9-11)</sup>. The (100) reflection decreased but the (200) reflection, (which is not shown here) increased slightly. In Fig. 3, it can be seen also that changes occurring in those crystallites contributing to the (100) reflection (a axis perpendicular to the film surface) and those crystallites contributing to the (020) reflection (b axis perpendicular to the film surface) occur at different rates. The peak height of the (100) reflection decreased to ~1/3 of its initial value during the first 6 seconds of poling,

while the (020) reflection has undergone no significant change. At the end of 30 seconds of poling, the peak height of the (100) reflection is  $\sim 1/5$  its initial value, while the peak height of the (020) reflection is  $\sim 3/4$  its initial value. Time dependent changes in intensity can also be observed in the (110) reflection and the phase I (110) (200) reflection.

The x-ray diffraction scans taken in transmission mode (shown in Fig. 4) exhibit much smaller changes when compared to the reflection scans. Since the time dependent changes were quite small, only the scans for the unpoled sample and the sample poled for two hours are included. The most significant changes are; a small decrease in the (100) reflection, a larger increase in the (020) reflection, and a decrease in the phase I (110) (200) reflection. The time dependence of these changes could not be accurately determined. The reflection scans show that crystallites with their a axes perpendicular to the film surface transform rapidly to polar phase II as evidenced by the large decrease in intensity of the (100) reflection during the first six seconds of poling. Those crystallites with their b axes perpendicular to the film surface transform at a much slower rate, as evidenced by the slower change in intensity of the (020) reflection. In fact, after six seconds of poling, no significant change in the intensity of the (020) reflection has occurred. With these facts in mind, it appears quite plausible to assume that the rapid increase in film polarization (as suggested by the rapid increase in  $d_{31}$  and  $e_{31}$  shown

in Fig. 1 and Fig. 2) is due to the phase transition from phase II to polar phase II, for crystals with a perpendicular (or close to perpendicular) to the film surface. The slower increase in polarization during the next several hours of poling would be due to the completion of the phase transformation for these crystals and the much slower rate of transformation for crystals whose a axes are at some larger angle with respect to the normal to the film surface: For the biaxially oriented films used, the c axes are in the plane of the film.

The phase II crystal structure (see Fig. 5) has two chains in the unit cell. One of the chains has a large dipole moment component parallel to a and the other (symmetry related) chain has a large dipole moment component antiparallel to a. It has been suggested that the phase transition from phase II to polar phase II occurs by a 180° field-induced rotation of one of the chains, producing the structure shown in Fig. 6.<sup>9,10</sup> A simultaneous translation of the chain along c has also been suggested.<sup>9</sup>

If one accepts the theory that the phase transition is caused by the interaction between the applied poling field and the molecular dipoles, and given the data presented here which shows a time dependent phase transformation dependent on crystallite orientation, then the previously described relationship between crystallite orientation and phase transformation rate may be explained.

The driving force for the time dependent transformation would be

the interaction energy ( $u = -\underline{\mu} \cdot \underline{E}$ ) of the poling field ( $\underline{E}$ ) with the component of the molecular dipole moment perpendicular to the chain axis ( $\underline{\mu}$ ). The change in molecular interaction energy occurring during the phase transition (assuming  $180^\circ$  rotation of one molecule) is  $u = 2\mu E$  for molecules in crystals with  $\underline{a}$  perpendicular to the film surface (since  $\underline{E}$  is perpendicular to the film surface). As the angle,  $\phi$ , between  $\underline{a}$  and the normal to the film surface increases  $u$  decreases and the driving force for the phase transition decreases (reaching a minimum when  $\phi = 90^\circ$ ) implying that crystallites with  $\phi > 0$  may not transform as rapidly. However, for crystallites with  $\phi \sim 90^\circ$ , a  $180^\circ$  rotation of one chain would produce a very small energy decrease and for  $\phi = 90^\circ$ , no energy decrease at all. That these crystals do transform is evidenced by the decrease in the (020) reflection in reflection mode. One may therefore propose a different transition mechanism for these crystals;  $90^\circ$  rotation of both chains in the unit cell into the field direction. The change in interaction energy counting both chains in the unit cell would be  $2\mu E$  for both cases:  $\phi = 0$  and  $\phi = 90^\circ$ . However, the barrier for  $180^\circ$  rotation of one chain and for the cooperative  $90^\circ$  rotation of both chains in the unit cell should be very different.

The possibility for  $90^\circ$  rotation of both chains is indicated by the decrease in intensity of the (020) reflection in reflection mode and its increase in transmission mode: a pole figure analysis of the (020) reflection is needed to firmly establish that  $90^\circ$  rotation can occur.

The availability of two distinct transition mechanisms would account for the rapid decrease in the (100) reflection ( $\phi = 0$ ) and the much slower decrease in the (020) reflection ( $\phi = 90^\circ$ ) if the barrier

for  $180^\circ$  rotation of one chain were less than the barrier for  $90^\circ$  cooperative rotation of both chains in the unit cell. This simple picture of the rate dependence of the phase transition on crystallite orientation needs further investigation. Future temperature dependent studies of the poling time dependence of changes in the (100) and (020) poles (pole figure analysis) should provide an indication of the allowed transformations ( $180^\circ$ ,  $90^\circ$ , etc.) and information on the activation energy of the transformations.

#### Acknowledgment

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# FIGURE CAPTIONS

Figure 1 - A plot of the complex piezoelectric stress constant  $e_{31}^*$  versus poling time ( $E_p = 2 \times 10^6$  V/cm,  $T_p = 23^\circ\text{C}$ )

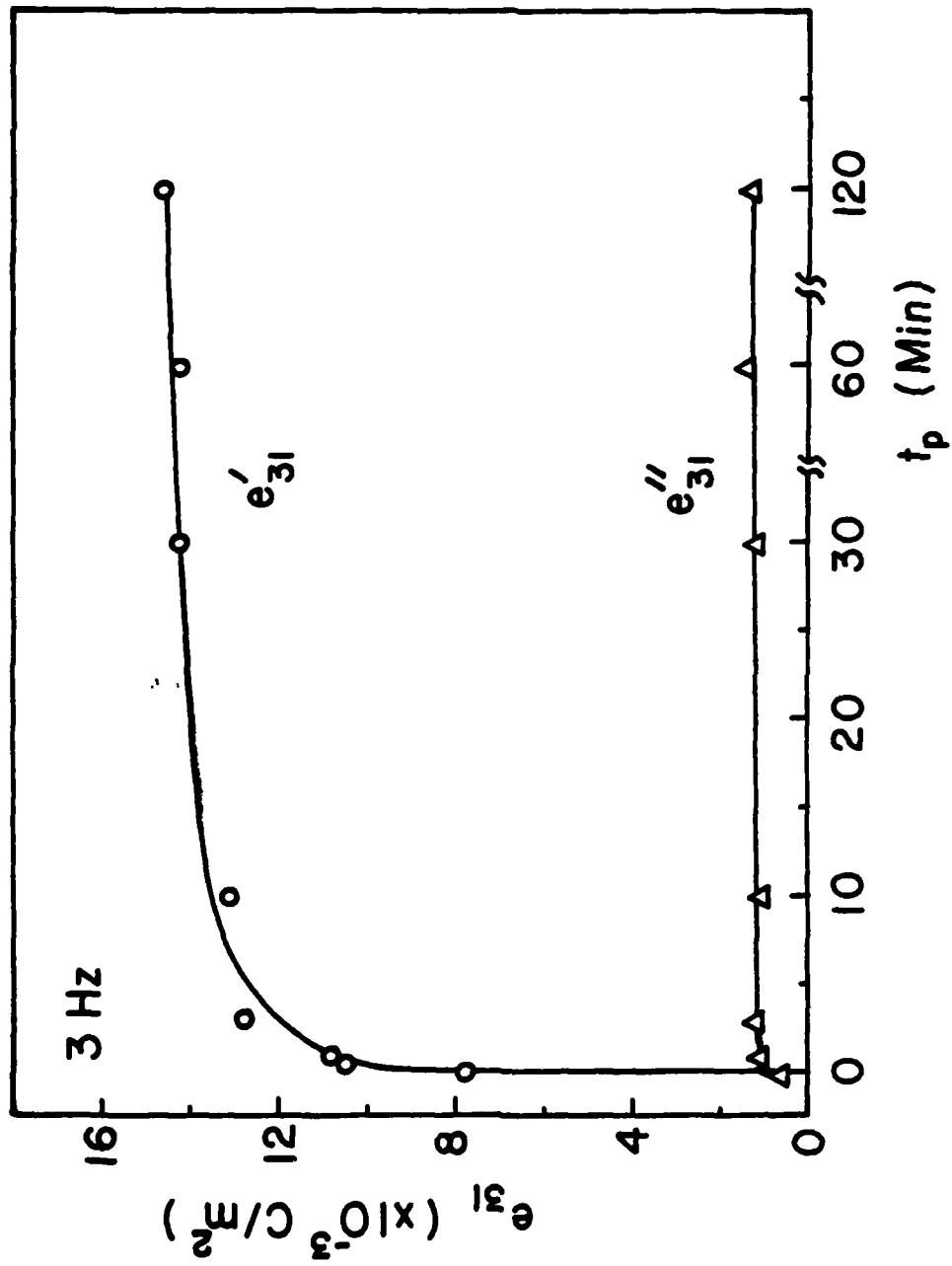
Figure 2 - A plot of the complex piezoelectric strain constant  $d_{31}^*$  versus poling time ( $E_p = 2 \times 10^6$  V/cm,  $T_p = 23^\circ\text{C}$ )

Figure 3 - Wide-angle x-ray diffractometer scans of samples poled for different poling times (reflection mode)

Figure 4 - Wide-angle x-ray diffractometer scans of unpoled sample and sample poled for two hours (transmission mode)

Figure 5 - C axis projection of phase II unit cell

Figure 6 - C axis projection of polar phase II unit cell



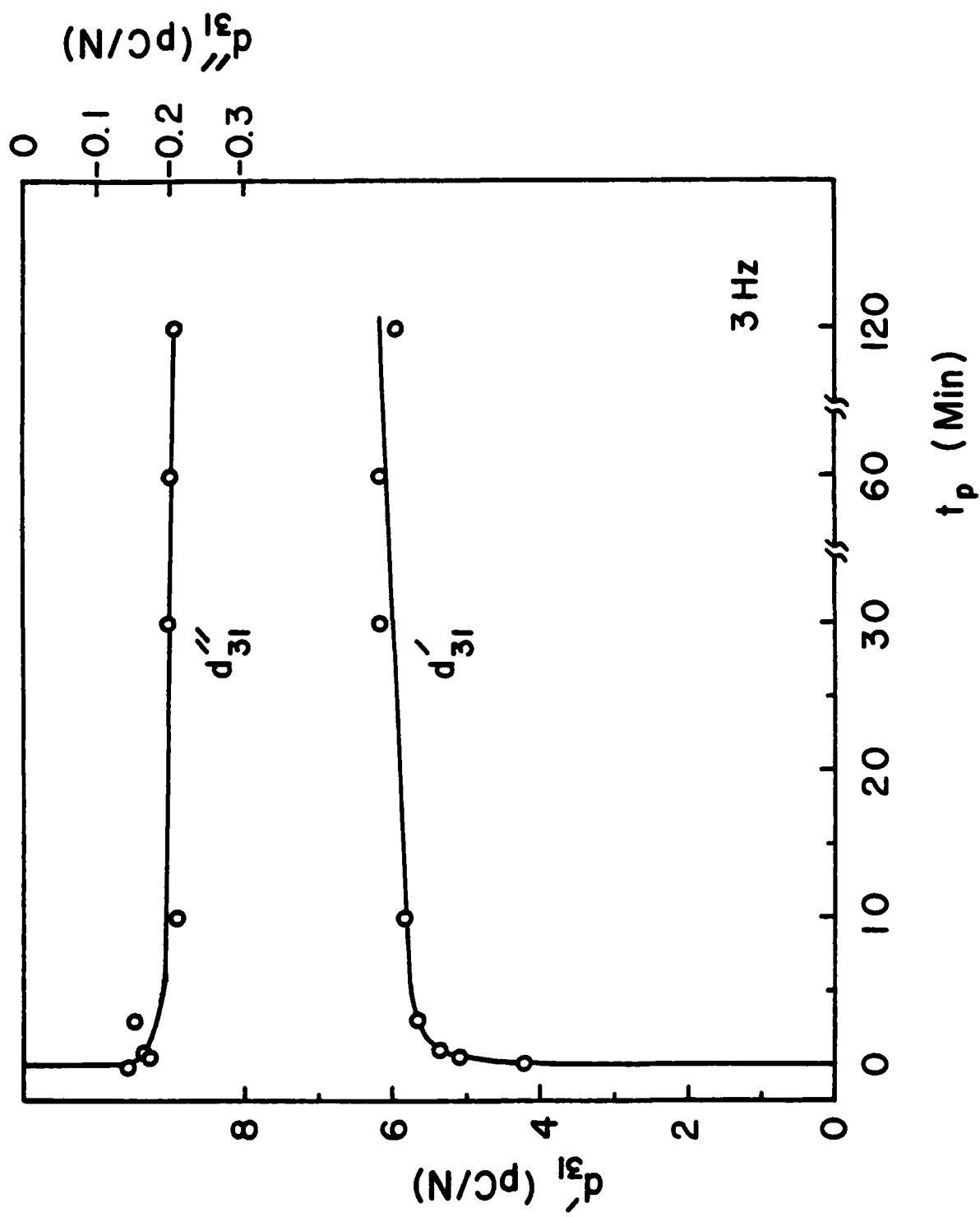
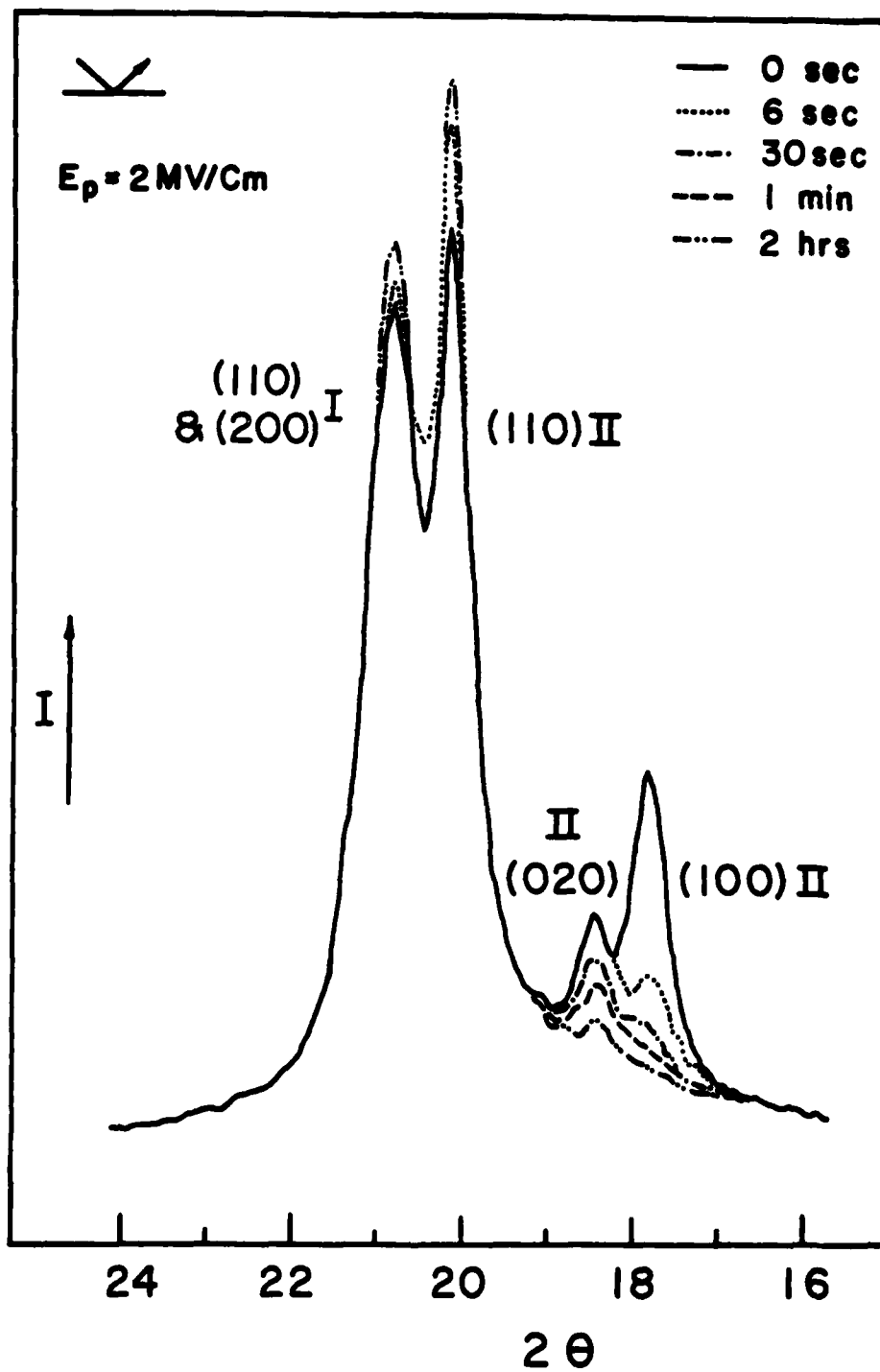
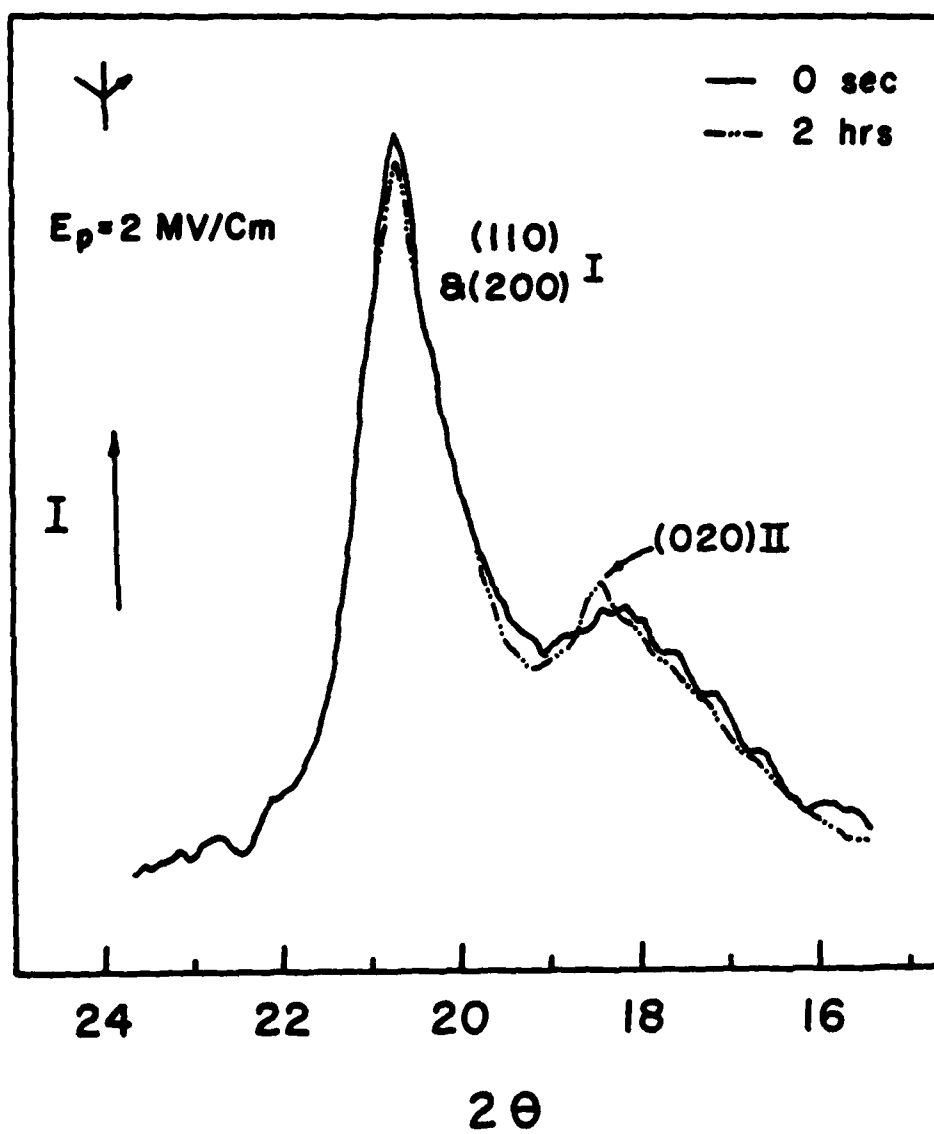
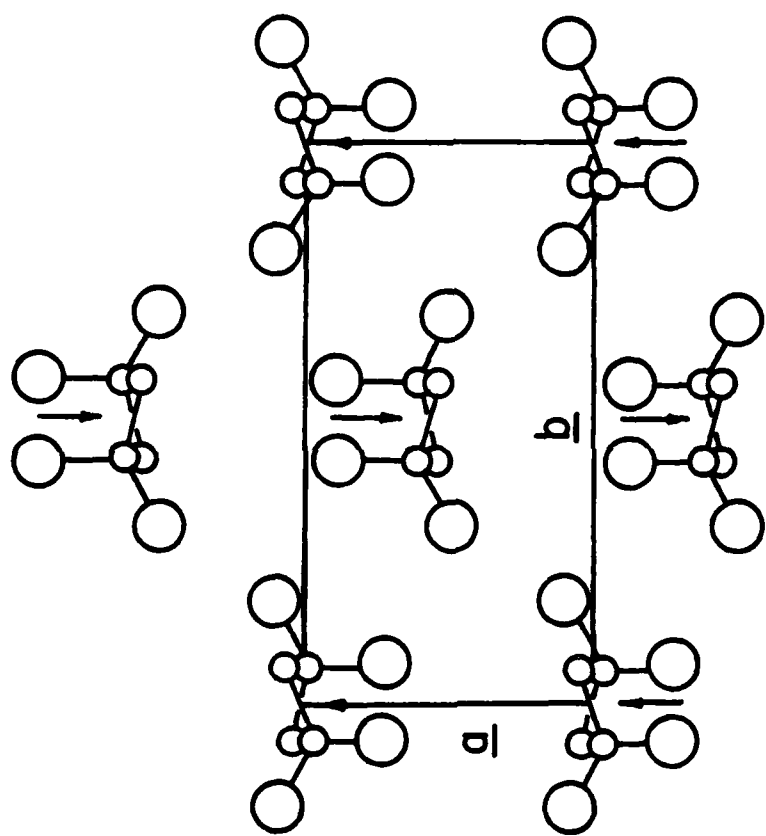


Fig 2







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